Journal of Electroanalytical Chemistry 690 (2013) 74–82

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Preparation and electrochemical behavior of the CA/TiO_2/Sb_2O_5 composite electrode modified with p-benzoquinone

Andrea Anilda Hoffmann da Rocha [a], Elisangela Bueno Pires [a], Aline da Silveira Nectoux [a], Silvio Luis Pereira Dias [a,*], Éder Claudio Lima [a], Cláudio Radtke [a], Lauro Tatsuo Kubota [b]

[a] Instituto de Química – UFRGS, CEP 91501-970, Porto Alegre RS, Brazil
[b] Universidade Estadual de Campinas – UNICAMP, Campinas SP, Brazil

ARTICLE INFO

Article history:
Received 12 September 2012
Received in revised form 29 October 2012
Accepted 2 November 2012
Available online 6 December 2012

Keywords:
p-Benzoquinone
Modified cellulose acetate
Titanium dioxide
Antimony pentoxide
Carbon paste electrode
Ascorbic acid

ABSTRACT

In this present study, a novel material made up of p-benzoquinone (BQ) immobilized on a new composite of cellulose acetate and mixed metal oxides (CA/TiO_2/Sb_2O_5) was applied to the electrocatalytic oxidation of ascorbic acid (H_2AA). The material was prepared by a phase inversion process and characterized by several techniques including scanning electronic microscopy coupled with energy dispersive spectroscopy (SEM–EDS), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence. Ti and Sb mapping profiles on the surface showed a homogeneous distribution of the matrices. Ti_{2p} and Sb_{3d} doublet indicate that the formation of TiO_2 and Sb_2O_5 is the presumed responsible for the good rigidity of the polymeric matrix. A carbon paste electrode of this material was used to study the electrocatalytic oxidation of ascorbic acid by cyclic voltammetric, chronoamperometric and differential pulse techniques. The electrode had a quick response time, showing great potential to be utilized as an electrochemical sensor for the determination of ascorbic acid in commercial samples.

1. Introduction

Supported mixed metal oxides on bio-based materials appear as an interesting alternative method for the immobilization of electroactive catalysts, since it may combine the advantages of mixed oxides with those of environment-friendly natural biopolymers [1].

In particular, the combination of a metal oxide with a natural biopolymer may offer several advantages, such as improved mechanical strength, high chemical and thermal stability, high ionic conductivity and strong surface acidity of metal oxides from renewable sources, not depending on petroleum sources, biodegradable, good biocompatibility, chemical inertness, relatively low cost, thermal stability and easy processing of cellulose and its derivatives [1–10]. Moreover, an additional advantage is referred to the method of preparation which allows obtaining a material in which the components are highly and homogeneously dispersed in biopolymeric matrix, which, by its turn, can be easily molded into different forms, such as membranes, fibers and spheres. These modified materials are normally made by mixing the cellulose acetate (CA) and metal alkoxide solutions followed by a phase inversion process [11,12].

So far, a number of papers have been published on cellulose acetate–metal oxides (CA/M_xO_y) hybrids or composites [13–41]. CA/M_xO_y hybrids or composites materials have been used in relevant applications, including various combinations of cellulose acetate with metal oxides such as ZnO, Cu_2O, Al_2O_3, TiO_2, ZrO_2, and Nb_2O_5, in ion exchange process [12–14], adsorption processes [15–19], kinetic studies [20], photocatalysis [21–25], as substrates for enzyme immobilization [26–30], as semi-permeable membranes [31], ultrafiltration process [32,33], biological process [34], proton conductors batteries [35], and in the immobilization of electroactive species, aiming to prepare modified electrodes [36–41].

However, in the field of electroanalysis, the use of chemically modified electrodes (CMEs) based in cellulose acetate–metal oxide composite materials as solid supports has received little attention when compared with others inorganic support materials such as silica gel, sol–gel and zeolites [42–51]. This can be attributed to the inherent disadvantages of bio-based materials such as the relatively low tensile resistance, hydrophilicity, high swellability, lower softening temperature and poor solubility in common solvents, which have limited their wider applications [52–54]. To overcome such drawbacks, the controlled physical and/or chemical modification of the cellulose acetate structure is necessary. Accordingly, inorganic polymeric materials with chemical and thermal stability may be substituted by less expensive and more versatile composite materials based on cellulose acetate–metal oxide supports.

The unique combination of the metal oxide particulates dispersed inside and outside of an inert biopolymer material appears interesting for the preparation of chemically modified electrodes

* Corresponding author. Tel.: +55 51 3308 7175; fax: +55 51 3308 7304.
E-mail address: silviol@ufrgs.br (S.L.P. Dias).

1572-6657/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2012.11.019

due to their excellent electron transfer properties. The phase inversion process can provide amorphous porous mixed oxides such as TiO_2/Sb_2O_5, in which the TiO_2 is dispersed throughout the bulk while the Sb_2O_5 covers only the matrix surface as a monolayer film prepared by a grafting technique [55]. The structural characteristics of the mixed metal oxide can differ greatly from those of the pure oxides. The high density of Brönsted and Lewis acid sites on these binary oxide surfaces allow preparing a series of electrochemical sensors and biosensors whose main characteristics are improved selectivity and sensitivity [56].

On the basis of the characteristics mentioned above, our research group has devised a new composite which can be used as an electrode material whose electrochemical behavior and electroanalytical performance are discussed hereinafter. The new CA/TiO_2/Sb_2O_5 composite material combines both the favorable conductivity and ion the exchange properties of mixed metal oxides with the attractive advantages of cellulose acetate processing, thus becoming a new type of promising material for electrodes. In addition, this composite material was modified with p-benzoquinone (BQ) and, subsequently, the CA/TiO_2/Sb_2O_5/BQ modified electrode was used in the electrocatalysis and determination of ascorbic acid (H_2AA) in aqueous buffer solution by cyclic voltammetry, amperometric detection and differential pulse voltammetry.

2. Experimental

2.1. Chemical and solutions

All chemicals were of analytical grade and used without additional purification. Graphite powder (99.9%) and mineral oil were purchased form Aldrich, Milwaukee-USA. Britton–Robinson (B–R) (acetic, phosphoric, boric acids) were acquired form Sigma, St. Louis, USA. Titanium terc-butoxide, $Ti[OC(CH_3)_3]_4$, antimony pentachloride, $SbCl_5$ 99% and p-benzoquinone, $C_6H_4(=O)_2$ 98% were obtained from Merck. The solutions were prepared by using deionized water and the pH values of the buffer solution were determined with a Mettler Toledo pHmeter FE20. Working standard solutions were freshly prepared by appropriate dilution of the stock solutions with deionized water.

2.2. Modification of the CA/TiO_2 composite

The CA/TiO_2 composite was prepared by phase inversion method whose procedures are described elsewhere [1,38,39,57].

About 10 g of CA/TiO_2 composite content 15.6 wt.% (1.7 mmol g^{-1}) TiO_2 incorporated in the cellulose acetate matrix were immersed in 300 mL of an acidic aqueous solution and 0.5 g (0.0016 mol) of $SbCl_5$. The mixture was stirred at 298 K for 3 h. The solid was filtered, washed with 1.0 mol L^{-1} HNO_3 solution in order to avoid Sb^{5+} hydrolysis and to eliminate chloride ions, and finally washed with deionized water until the washing solution achieved a pH 6.0. The sample obtained was designated as CA/TiO_2/Sb_2O_5.

2.3. Immobilization of p-benzoquinone on CA/TiO_2/Sb_2O_5

Aqueous solution of the p-benzoquinone, BQ, (Aldrich) was prepared in a concentration of 1.0×10^{-3} mol L^{-1} dissolved in isopropanol. An amount of 0.5 g of CA/TiO_2/Sb_2O_5 was added to 10 mL of BQ solution. The mixture was shaken for 30 min and the resulting solid was filtered, washed several times with bidistilled water and dried in an oven for 30 min at 60 °C. The material will hereafter be designated as CA/TiO_2/Sb_2O_5/BQ.

The quantify of the p-benzoquinone mediator immobilized on the CA/TiO_2/Sb_2O_5 surface was determined by ultraviolet spectra using a Shimadzu – UV1601PC spectrophotometer. Absorbance measurements were made at the maximum wavelength of CR at 294 nm.

2.4. EDS analysis

The EDS image was obtained for CA/TiO_2/Sb_2O_5 material dispersed on a conductive double-sided tape on an aluminum support and coated with a thin carbon film using a Baltec SCD 050 Sputter Coater apparatus. The micrograph was obtained using a Jeol Scanning Electron Microscope, model JSM 5800, connected to a secondary electron detector and X-ray energy dispersive spectrometer (EDS) for elemental mapping in a Noran Instrument. The image was obtained with a magnification of 1000×.

2.5. X-ray fluorescence

The amount of TiO_2 and Sb_2O_5 immobilized in the cellulose acetate matrix was determined by X-ray fluorescence using a Spectrace model 5100, EDXRF spectrometer.

2.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed in an Omicron-SPHERA station using Al Kα radiation (1486.6 eV). The anode was operated at 225 W (15 kV, 15 mA). Survey spectra were recorded with a 50 eV pass energy. The Sb 3*d* and Ti 2p regions were recorded with a higher resolution (pass energy of 20 eV). The detection angle of the photoelectrons (Θ) with respect to the sample surface (take-off angle) was fixed at 53° for all measurements. The *C* 1s signal from adventitious carbon at 285 eV was used as an internal energy reference. All spectra were fitted assuming a Shirley background. Lines were fitted by 70% Gaussian + 30% Lorentzian functions with set values of full width at half maximum for each line.

2.7. Electrode preparation and electrochemical measurements

The carbon paste electrode was prepared by mixing 20 mg of the material CA/TiO_2/Sb_2O_5/BQ with 20 mg of analytical grade graphite (Aldrich, 99.9%) and a drop of liquid paraffin as a binder. This paste was placed in a 1-mm-deep cavity, in contact with a 5 mm internal diameter platinum disk which is fused to a glass tube. The carbon paste electrodes made with the CA/TiO_2/Sb_2O_5/BQ material were used as working electrodes, a platinum wire served as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The studies were carried out in Britton–Robinson (B–R) universal buffer aqueous solution prepared with equimolar amounts (0.4 mol/L) of acetic, phosphoric, boric acids at constant ionic strength (1.0 mol/L KCl) adjusted to the required pH with 0.2 mol/L NaOH or HCl solution. All experiments were conducted at room temperature (25 ± 2 °C). Nitrogen gas was bubbled through the electrolyte solution before the electrochemical measurements, and a gentle gas flow was kept above electrolyte surface during the experiment. The ascorbic acid solution was freshly prepared before using it.

Cyclic voltammetry studies were carried out in an Ivium Stat electrochemical analyzer (serial number A08044) under computer control. The electrocatalytic oxidation of H_2AA by the CA/TiO_2/Sb_2O_5/BQ carbon paste electrode was investigated by cyclic voltammetry (CV), pulse differential (DP) and amperometric detection (AD) techniques, adding freshly prepared ascorbic acid solutions into the electrochemical cell containing 20 mL of the buffer solution.

3. Results and discussion

3.1. Characteristics of the material

The combination of mixed metal oxides with bio-based materials like these cellulose derivatives is an interesting alternative that can generate new and versatile catalytic supports for efficient immobilization of electroactive catalysts. The CA/TiO_2/Sb_2O_5 and CA/TiO_2/Sb_2O_5/BQ materials were characterized by using SEM, EDS and XPS techniques.

The Fig. 1 shows the SEM and EDS images obtained for the CA/TiO_2/Sb_2O_5 material. The scanning electron microscopy (SEM) micrographs of CA/TiO_2/Sb_2O_5 presented in Fig. 1A, within the established magnification, show that there are no distinguishable separated phases and agglomerated titanium and antimony particles were not detected. However, the material shows regions with several cavities due to degradation caused by acid attack. Moreover, when the $SbCl_5$ was incorporated in the CATiO_2, formation of a dense layer of hydrated oxide generated by hydrolysis is observed. The elemental EDS analysis presented in Fig. 1B and C shows high titanium and antimony content over the cellulose acetate surface, respectively. The Ti/Sb percent composition found was 15.6%TiO_2 and 3.0%Sb_2O_5. From the energy dispersive image (Fig. 1B) it was possible to observe that the titanium and antimony dispersion was very uniform. The bright points observed in Fig. 1B and C is due to the titanium (Ti Kα = 4.5 keV) and antimony atoms (Sb Lα = 3.6 keV). At the chosen magnification, the EDS image is indicating that the metals are homogeneously dispersed over the cellulose acetate fiber.

Fig. 2A shows the XPS spectrum of the Sb 3*d* region obtained from the CA/TiO_2/Sb_2O_5 material. The Sb 3*d* doublet was simulated by two lines with a branching ratio $3d_{5/2}/3d_{3/2}$ of 1.5 (the statistical ratio) and a spin-orbit splitting of 9.5 eV. The Sb $3d_{5/2}$ line has a binding energy (BE) of 530.5 eV, which corresponds to Sb in a Sb_2O_5 oxide. Ti chemical environment was probed by analyzing the Ti 2*p* region. The BE of the Ti $2p_{3/2}$ line (Fig. 2B) is 458.5 eV, which corresponds to TiO_2.

The dispersion of the TiO_2 throughout the bulk of cellulose acetate and the incorporation of Sb_2O_5 on the matrix surface can be described according to the following proposed reaction based on the titanium antimonate phase formation.

$$n\mathrm{CAOH} + \mathrm{Ti}[\mathrm{OC}(\mathrm{CH_3})_3]_4 \rightarrow (\mathrm{CAO})_n\mathrm{Ti}[\mathrm{OC}(\mathrm{CH_3})_3]_{4-n} + n\mathrm{C_4H_9OH} \quad (1)$$

$$(\mathrm{CAO})_n\mathrm{Ti}[\mathrm{OC}(\mathrm{CH_3})_3]_{4-n} + (4-n)\mathrm{H_2O} \rightarrow (\mathrm{CAO})_n\mathrm{Ti}(\mathrm{OH})_{4-n} + (4-n)\mathrm{C_4H_9OH} \quad (2)$$

$$n\mathrm{CAO/TiOH} + (\mathrm{HO})_n\mathrm{Sb}(\mathrm{OH})_{5-n} \rightarrow (\mathrm{CAO/TiO})_n\mathrm{Sb}(\mathrm{OH})_{5-n} + n\mathrm{H_2O} \quad (3)$$

The contents of TiO_2 and Sb_2O_5 incorporated in the cellulose acetate matrix were determined to be 15.6 wt.% and 3.0 wt.%, respectively, using X-ray fluorescence. This matrix, CA/TiO_2/

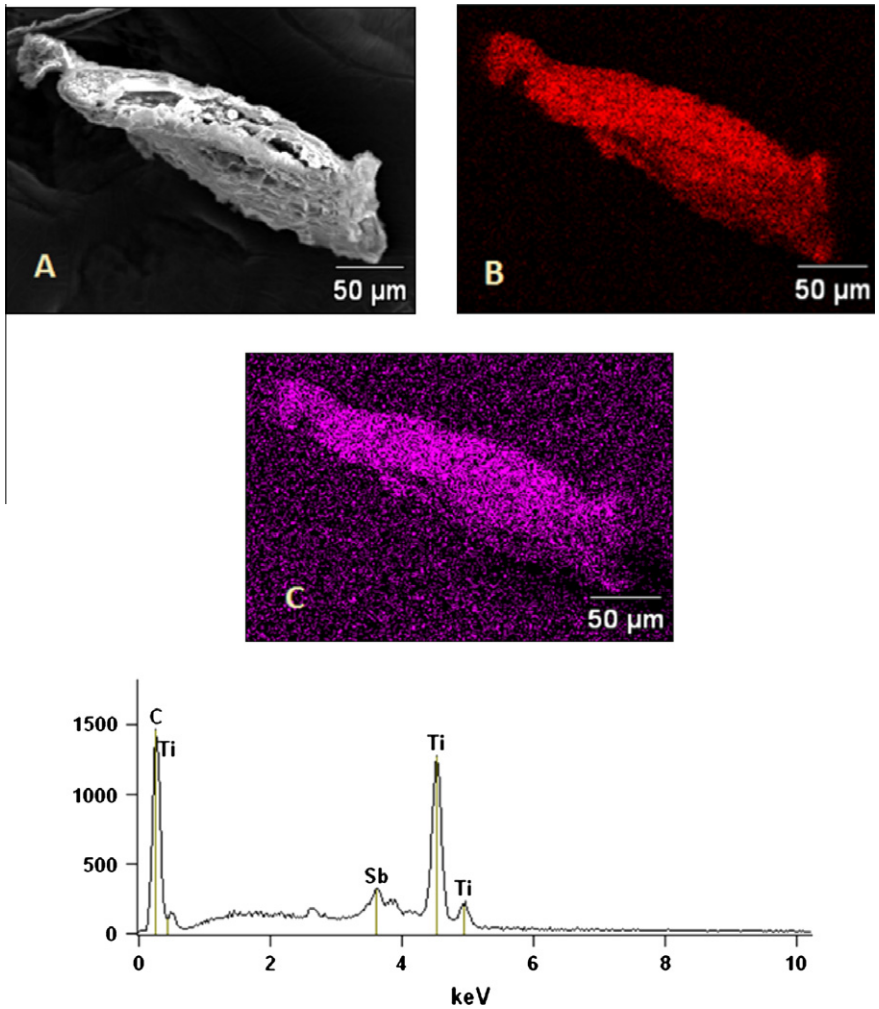

Fig. 1. Scanning electron micrographs of CA/TiO_2/Sb_2O_5 (A), and the corresponding energy dispersive scanning images (EDS) of titanium (B) and antimony (C).

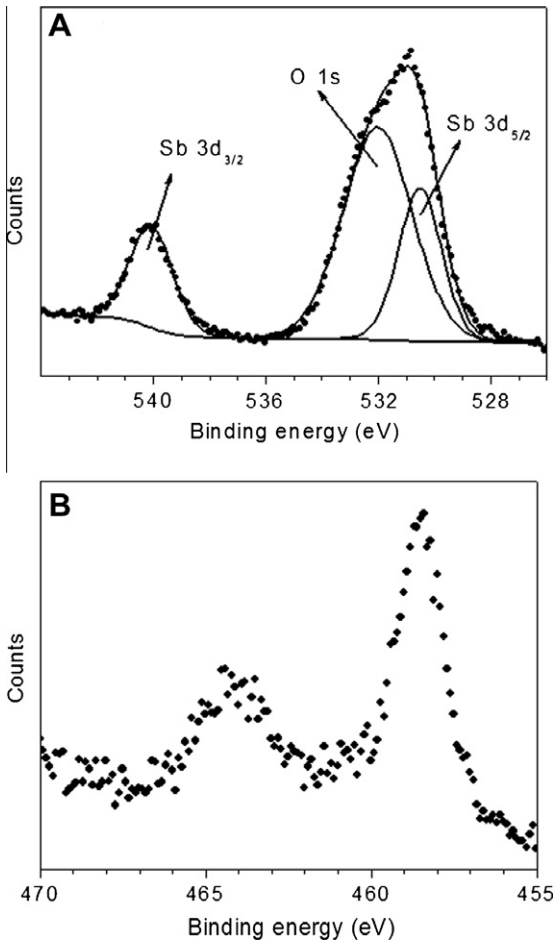

Fig. 2. (A) Sb 3*d* region of the XPS spectra of $CA/TiO_2/Sb_2O_5$ material. Points represent experimental data. Solid curves correspond to background, fitting components, and their sum; (B) Ti 2p region of the XPS spectra of $CA/TiO_2/Sb_2O_5$ material.

Sb_2O_5, was then used for the immobilization of the BQ. The BQ molecule is a ring of six carbons, non-aromatic, corresponding to the oxidized form of hydroquinone which presents reversible redox properties, involving two protons and two electrons. The redox process occurs in the carbonyl groups in the positions 1 and 4 of the BQ structure as showed by the following expression:

The amount of mediator immobilized on the $CA/TiO_2/Sb_2O_5$ surface was calculated by applying the equation:

$$q = \frac{(C_0 - C_e)}{m} \cdot V \quad (4)$$

where q is the amount of p-benzoquinone mediator immobilized on the $CA/TiO_2/Sb_2O_5$ surface (mg g^{-1}); C_0 is the initial BQ concentration put in contact with the $CA/TiO_2/Sb_2O_5$ material (mg L^{-1}), C_e is the BQ concentration (mg L^{-1}) after the stirring process, m is the mass of $CA/TiO_2/Sb_2O_5$ material (g) and V is the volume of mediator put in contact with the $CA/TiO_2/Sb_2O_5$ material. The amounts of p-benzoquinone adsorbed onto $(CAO/TiO)_nSb(OH)_2$ were determined by ultraviolet spectra, resulting in 21.6 ± 0.4 mg g^{-1}.

The immobilization of p-benzoquinone molecule on $CA/TiO_2/Sb_2O_5$ surfaces should occur by an ion exchange reaction, represented in a simplified manner by the following reaction:

$$(CAO/TiO)_nSb(OH)_2 + BQ^+_{ox} \rightarrow (CAO/TiO)_nSbO^-BQ^+_{ox} + 2H^+ \quad (5)$$

3.2. Electrochemical behavior of the $CA/TiO_2/Sb_2O_5$/BQ composite electrode

Fig. 3 shows the cyclic voltammograms obtained using a carbon paste electrode modified with the matrix $CA/TiO_2/Sb_2O_5$ in the Britton–Robinson buffer solution (pH 7.0) at a scan rate of 20 mV s^{-1} (A) without and (B) with p-benzoquinone adsorbed on its surface. The voltammogram recorded with the unmodified electrode revealed a low background current and no peak in the scanning potential range (−0.4 and 0.7 V versus SCE), indicating no redox process at the electrode surface. However, using a carbon paste electrode modified with $CA/TiO_2/Sb_2O_5$/BQ, an enhancement

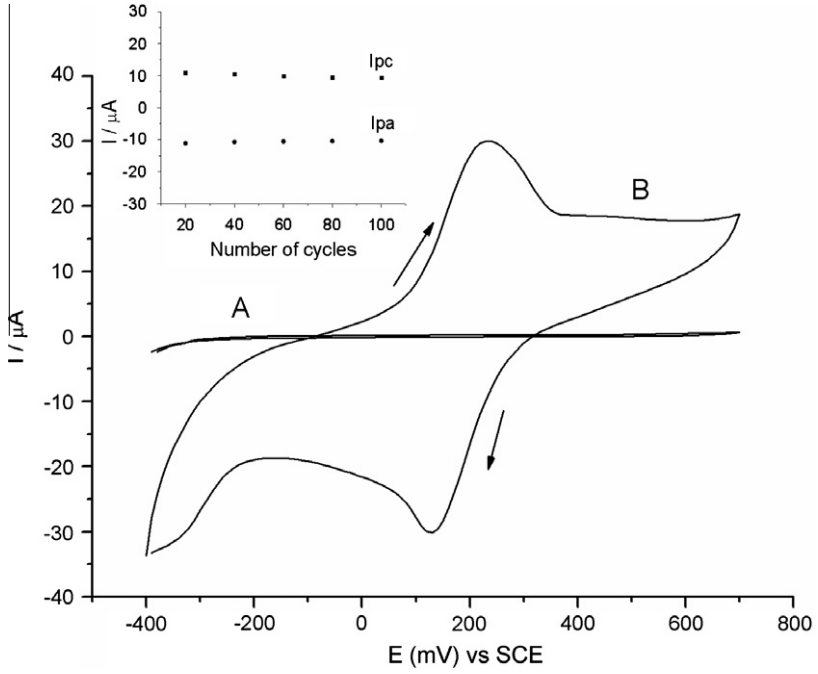

Fig. 3. Cyclic voltammograms of the $CA/TiO_2/Sb_2O_5$ electrode (A) and of the $CA/TiO_2/Sb_2O_5$/BQ modified electrode (B) in scan rate at 20 mV s^{-1}, 1.0 mol L^{-1} Britton–Robinson buffer solution, at pH 7.0. Inserted figure shows chemical stability of $CA/TiO_2/Sb_2O_5$/BQ electrode under various redox cycles.

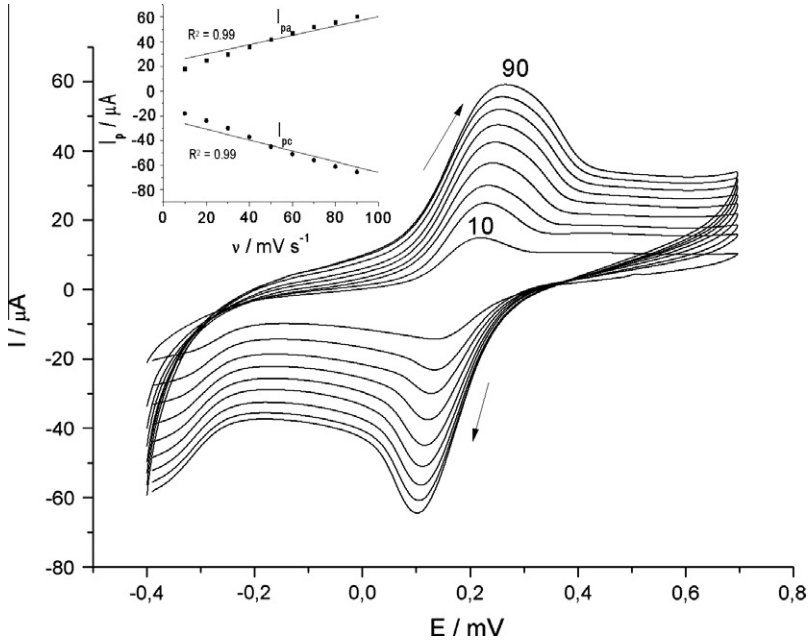

Fig. 4. Cyclic voltammograms obtained at different scan rates (2, 5, 8, 10, 20, 30, 40, and 50 mV s^{-1}), in 1.0 mol L^{-1} Britton–Robinson buffer solution, at pH 7.0. Inserted figure shows the plot of the cathodic and anodic peak currents, I_{pc} and I_{pa}, versus scan rate, v.

of the current, with well-defined anodic and cathodic peak currents, is observed, reflecting an electrochemically active redox couple. The formal midpoint potential, $E^{0'}$ ($E^{0'} = E_{pa} + E_{pc})/2$ where E_{pa} is the anodic peak potential of 234 mV and E_{pc} is the cathodic peak potential of 128 mV, respectively, was 180.5 mV for CA/TiO_2/Sb_2O_5/BQ. This behavior suggests that the interaction between the oxidized form of BQ and the matrix CA/TiO_2/Sb_2O_5 is stronger than the one observed for the reduced form. A possible explanation for this behavior can be attributed to electrostatic attractions involving oxygen atoms present in the p-benzoquinone molecules with metal oxides dispersed over the cellulose acetate fiber. Based on the charge under the voltammetric peaks, considering that the geometric area of the electrode is 0.28 cm^2 and assuming that two electrons were involved in the redox process, a surface coverage of approximately 7.95×10^{-9} mol cm^2 was estimated. Also, the experimental results show that the peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc} = 98$ mV) is greater than the value of 59/n mV expected for a reversible system. This result may be related to the two-electron redox potential, with kinetic limitation. An anodic peak current (I_{pa}) of 30.3 µA and cathodic peak current (I_{pc}) of −30.0 µA, for a [I_{pa}/I_{pc}] of 1.08, describing this system as quasi-reversible electrochemically behavior, were also observed.

The stability of the CA/TiO_2/Sb_2O_5/BQ electrode was checked by successive recording of voltammograms (inserted in Fig. 3). After 100 cycles no changes were observed in the voltammetric profiles of the modified electrode, indicating that the electroactive species is bound to the surface according to the behavior described by Eq. (5).

Fig. 4 shows typical cyclic voltammograms of the CA/TiO_2/Sb_2O_5/BQ electrode obtained at scan rates in the range 10–90 mV s^{-1}. Plotting both the cathodic and the anodic peak currents versus v, where v is the scan rate (inserted in Fig. 4), a linear correlation is obtained (r = 0.99 and 0.99), as expected for the redox species confined on the electrode surface [59]. Moreover, the peak-to-peak potential separation, ΔE_p, was about 135 mV, which is consistent with a quasi-reversible electronic transfer kinetic.

The electrochemical process undergone by BQ in the solution phase is well-known [58]. The general mechanism of reduction of

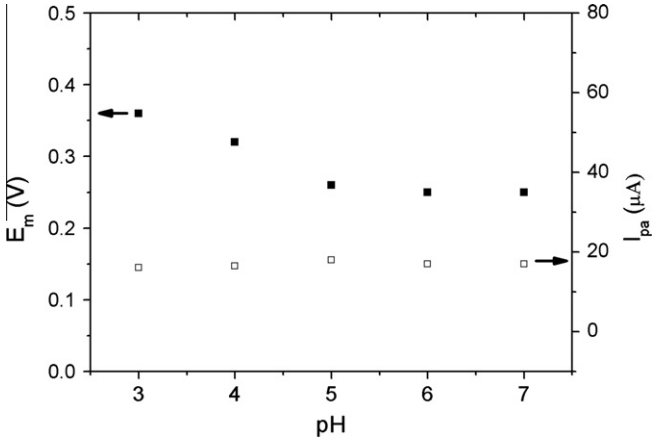

Fig. 5. Plot of the solution pH against E_m and I_{pa}. Measurements in 1.0 mol L^{-1} Britton–Robinson buffer solution, v = 20 mV s^{-1}, at pH 7.0.

quinone groups occurs by the transference of two electrons and two protons captured in a single step, which can produce a pH dependence and a displacement in the formal midpoint potential, E_m. The CA/TiO_2/Sb_2O_5/BQ modified electrode response was investigated in the pH range between 3.0 and 7.0, using the Britton–Robinson buffer as the supporting electrolyte solution (Fig. 5). This study showed that the anodic and cathodic peak currents, I_{pa} and I_{pc} are not affected, remaining practically constant in the investigated range of pH. The formal midpoint potential, E_m, of the surface redox pair, calculated as the average of the anodic and cathodic peak potentials, [$E_m = (E_{pa} + E_{pc})/2$] of the cyclic voltammograms recorded at a potential scan rate of 20 mV s^{-1} was pH-independent in the range 4.0–7.0. For pH values lower than 4.0, the formal midpoint potential undergoes displacements to more positive values. This fact reveals the acidic character of the matrix, allowing the process to be independent of the pH of the medium until pH 4.0 is reached. Below this value the matrix effect is minimized, suggesting that the protection is not sufficient to prevent the participation of the proton in the redox process.

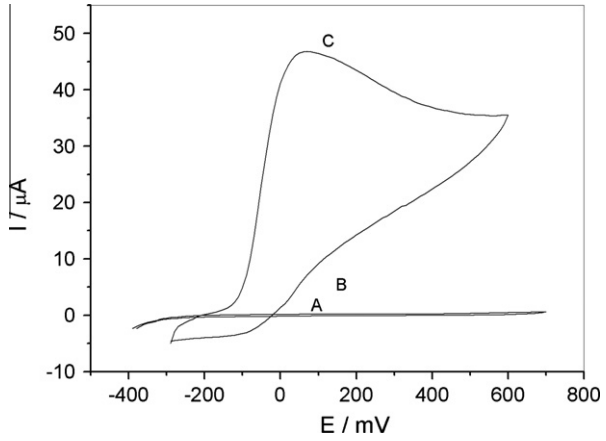

Fig. 6. Cyclic voltammograms curves for the CA/TiO_2/Sb_2O_5/BQ modified electrode in the absence and presence of ascorbic acid for: CA/TiO_2/Sb_2O_5 (A) and CA/TiO_2/Sb_2O_5/BQ (B) in the absence of the H_2AA; CA/TiO_2/Sb_2O_5/BQ (C) in the presence of 8.50×10^{-5} mol L^{-1} ascorbic acid. Measurements in 1.0 mol L^{-1} Britton–Robinson buffer solution, $v = 20$ mV s^{-1}, at pH 7.0.

3.3. Electrochemical behavior of the CA/TiO_2/Sb_2O_5/BQ electrode in the presence of H_2AA

The electrocatalytic peak current of ascorbic acid oxidation at the surface of the CA/TiO_2/Sb_2O_5/BQ modified electrode can be used in the determination of ascorbic acid in aqueous solution. Amperometric detection (AD), cyclic voltammetry (CV), and differential pulse voltammetry (DP) methods were used to evaluate the electrochemical behavior and analytical performance of the CA/TiO_2/Sb_2O_5/BQ modified electrode as an electrochemical sensor for ascorbic acid in the presence of four possible interfering substrates.

Fig. 6 shows cyclic voltammetric experiments performed with the CA/TiO_2/Sb_2O_5/BQ modified electrode in the absence and presence of 8.50×10^{-5} mol L^{-1} ascorbic acid in 1.0 mol L^{-1} Britton–Robinson buffer solution, $v = 20$ mV s^{-1}, at pH 7.0. Comparing this voltammogram to that obtained in the absence of H_2AA, a drastic enhancement of the anodic peak current is observed, confirming a very strong electrocatalytic response (*C*). Another confirmation of the electrocatalytic process is the non-existence of a cathodic process, which can be viewed as a consequence of the consumption of the oxidized form of the mediator by the substrate.

The amperometric detection technique was employed to the investigation of electrode processes at chemically modified electrodes setting the working electrode potential into the electrochemical cell at $E_{pa} = 0.300$ V, pH 7.0 (not provided data). In the range of ascorbic acid concentrations between 1.5×10^{-5} and 1.2×10^{-4} mol L^{-1}, the adjusted equation (inserted Figure) for the linear response range was $I/\mu A = (1.12 \pm 0.07) + (40.1 + 0.95)$ [H_2AA]/mmol L^{-1} ($r = 0.996$, $n = 28$). The achieved detection limit (3 standard deviations of the blank divided by the slope of calibration curve) was 26 μmol L^{-1}, quantification limit (10 standard deviations of the blank divided by the slope of calibration curve) was 87 μmol L^{-1} and sensitivity 40.1 μA cm^{-2} mmol L^{-1}.

For more information about electro-oxidation, the amperometric detection was used for the estimation of the diffusion coefficient of ascorbic acid in aqueous solution using the CA/TiO_2/Sb_2O_5/BQ modified electrode.

The diffusion-controlled current is expressed by the Cottrell equation [59]:

$$j = nFAD^{1/2}C_s\pi^{-1/2}t^{-1/2} \quad (6)$$

where n is the number of electrons transferred, F is the Faraday constant, A the electrode area in cm^2, D is the diffusion coefficient (cm^2 s^{-1}), C_s ascorbic acid bulk concentration in mol cm^{-3}, respectively. Fig. 7A shows the chronoamperograms obtained in the absence and presence of four different concentrations of ascorbic acid.

As can be seen in the Fig. 7B, a plot of I versus $t^{-1/2}$ shows a linear relation, indicating that the electrocatalytic current observed must be controlled by the diffusion of ascorbic acid from the bulk solution towards the surface of the electrode causing a near Cottrellian behavior. A plot of the slopes of such lines versus H_2AA concentration (Fig. 7C) can be used to estimate the diffusion coefficient of ascorbic acid in the ranges of 15–60 μmol L^{-1}. The

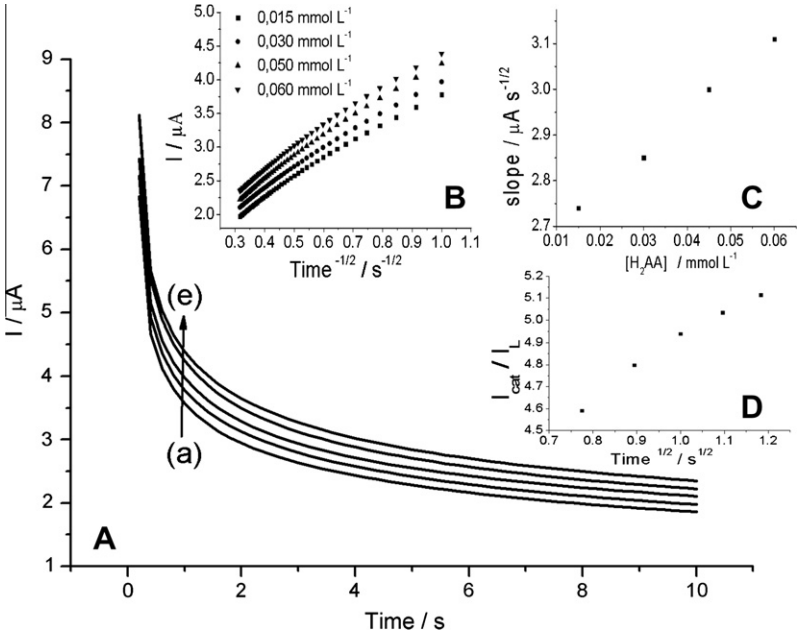

Fig. 7. (A) Amperometric detection curves obtained at the CA/TiO_2/Sb_2O_5/BQ modified electrode in 1.0 mol L^{-1} Britton–Robinson buffer solution, at pH 7.0 for different ascorbic acid concentrations at an applied potential of 0.300 V. (B) Plots of I versus $t^{-1/2}$ obtained from chronoamperograms. (C) Plot of the slope of straight lines versus the ascorbic acid concentration. (D) Plot I_{cat}/I_L versus $t^{1/2}$ derived from the data of chronoamperograms of (a) and (c).

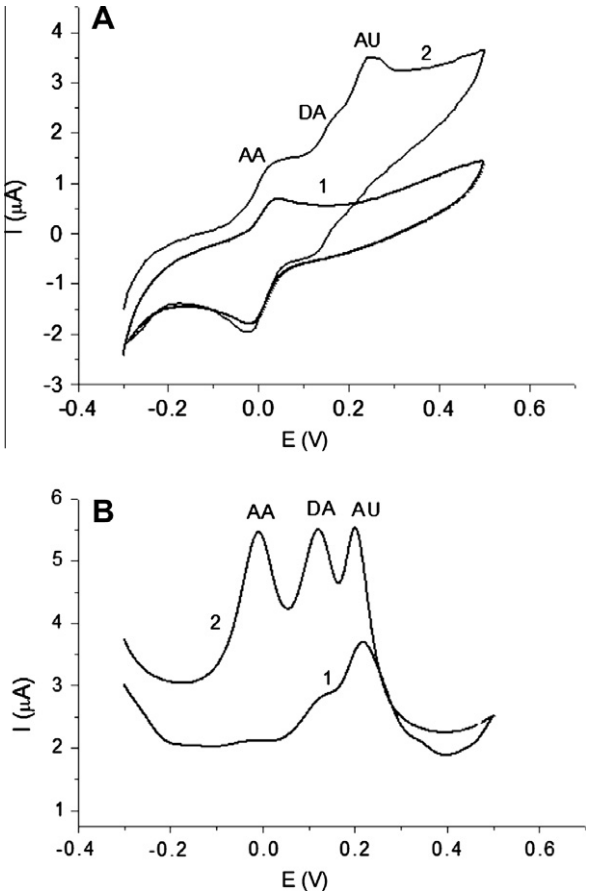

Fig. 8. (A) Cyclic voltammograms curves for the CA/TiO_2/Sb_2O_5 (1) and CA/TiO_2/Sb_2O_5/BQ (2) modified electrode, in presence 5.0×10^{-5} mol L^{-1} H_2AA, 1.1×10^{-4} mol L^{-1} DA, 5.0×10^{-5} mol L^{-1} UA. Measurements in 1.0 mol L^{-1} Britton–Robinson buffer solution, $v = 20$ mV s^{-1}, at pH 7.0. (B) Differential pulse voltammograms curves for the CA/TiO_2/Sb_2O_5 (1) and CA/TiO_2/Sb_2O_5/BQ (2) modified electrode in presence 5.0×10^{-5} mol L^{-1} H_2AA, 1.11×10^{-4} mol L^{-1} DA, 5.0×10^{-5} mol L^{-1} UA in 1.0 mol L^{-1} Britton–Robinson buffer solution, $v = 10$ mV s^{-1}, amplitude 50 mV, at pH 7.0.

mean value of D was found to be 2.84×10^{-6} cm^2 s^{-1}, comparable with those reported previously [60].

Also, the amperometric detection technique was employed to evaluate the catalytic rate constant, k, for the reaction between ascorbic acid and the CA/TiO_2/Sb_2O_5/BQ electrode according to the method of Galus [61]:

$$I_{cat}/I_L = \pi^{1/2}(kC_s t)^{1/2} \quad (7)$$

where I_{cat} and I_L are the currents of the modified electrode in the presence and absence of ascorbic acid, respectively, k is the catalytic rate constant (cm^{-3} mol^{-1} s^{-1}), C_s is the concentration of ascorbic acid (mol L^{-1}) and t is the elapsed time (s). The above equation can be used to calculate the rate constant of the catalytic process k. Based on the slope of the I_{cat}/I_L versus $t^{1/2}$ plot, the value of k can be obtained for a given ascorbic acid concentration (Fig. 7D). The mean value for k was found to be 2.0×10^4 L mol^{-1} s^{-1} between 15 and 60 μmol L^{-1} concentrations of ascorbic acid. Therefore, the observed behavior is compatible with an electrocatalytic process for electro-oxidation of ascorbic acid at surface of the modified electrode and the k value explains the sharp feature of the catalytic peak observed for electro-oxidation of the CA/TiO_2/Sb_2O_5/BQ modified electrode [62].

The analytical performance of the CA/TiO_2/Sb_2O_5/BQ modified electrode were evaluated by cyclic voltammetry (CV), and differential pulse voltammetry (DP) techniques measuring successive additions of aliquots of the H_2AA into the electrochemical cell kept at E_{pa} = 0.300 V, in 1.0 mol L^{-1} Britton-Robinson buffer electrolyte solution, $v = 20$ mV s^{-1}, pH 7.0. Cyclic voltammetric and differential pulse voltammograms scans using H_2AA in the concentration ranges of 2.50×10^{-5} mol L^{-1} to 3.82×10^{-3} mol L^{-1} and 2.0×10^{-7} mol L^{-1} a 9.0×10^{-7} mol L^{-1} ($r = 0.998$), respectively, showed a highly linear response, reflecting the influence of the modification of the CA/TiO_2/Sb_2O_5/BQ electrode with p-benzoquinone. The achieved detection limit (3σ/slope ratio) were 2.75×10^{-3} mol L^{-1} and 1.9×10^{-5} mol L^{-1}, the sensitivity were 14.1 μA cm^{-2} mmol L^{-1} and 1291.7 μA cm^{-2} mmol L^{-1} by CV and DP techniques, respectively. Thus, the electrocatalytic oxidation of H_2AA can be applied to the determination of ascorbic acid.

In order to demonstrate the catalytic oxidation of ascorbic acid in real samples using the CA/TiO_2/Sb_2O_5/BQ electrode, an experiment was performed in order to determine the ascorbic acid concentration in commercial pharmaceutical tablets by AD and DP techniques. Commercial tablets were dissolved in 500.0 mL of distilled water (solution A). A 10.0 mL aliquot of this solution (A) was, then, removed and diluted to 100 mL using bidistilled water (solution B). The pulse differential responses were obtained by adding 10.0 μL aliquots of solution B into a cell filled with 20.0 mL of a 1.0 mol L^{-1} Britton–Robinson buffer solution at pH 7.0 under nitrogen. The concentration of ascorbic acid in the commercial Vitamin C formulation, which prescribed amount is 1 g/tablet was evaluated about (1.03 ± 0.03 g/tablet) and (0.995 g/tablet) by amperometric detection and differential pulse voltammetry, respectively. These values are comparable with the iodometric standard titration method [63]. The results demonstrate the satisfactory accuracy of the CA/TiO_2/Sb_2O_5/BQ modified electrode and indicate that the presence of other substances in the Vitamin C tablets, such as citric acid, lemon flavor, orange flavor, sodium bicarbonate, sodium cyclamate and quinoline yellow, did not affect the determinations [64].

In order to determine the selectivity of the CA/TiO_2/Sb_2O_5/BQ modified electrode in real samples containing H_2AA, two possible interfering substrates which have biological importance were

Table 1
Comparison of the CA/TiO_2/Sb_2O_5/BQ modified electrode with others electrodes for the determination of H_2AA.

Electrode	Modified	Method	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	Sensitivity	References
GCE	Bi_2S_3 nanorods	Amperometry	1–1000	83	–	65
Au	T(DBHP)P-Cu/L-cys	VPD	10.2–1000	0.541	–	66
CP	Graphene	Amperometry	0.07	0.1–106	−3,31571 (A mmol L^{-1})	67
TiO_2 nanotube arrays	Gold NP	Amperometry	1–4000	0.1	46.8 (μA mmol L^{-1} cm^{-2})	68
GCE	Plu/ZnO-NPs	Amperometry	1–360	1	–	69
CP	SiO_2/SnO_2/Phosphate/MelB	Amperometry	0.4–2000	0.4	–	70
SiO_2/C	Nb_2O_5 film	VPD	99–2380	25.03	23.76 (μA mmol L^{-1})	71
		DPV	0.2–0.9	0.019	1291.7 (μA L $mmol^{-1}$)	This work
		Amperometry	15–120	26	40.1 (μA L $mmol^{-1}$)	
		CV	25–3800	2.8	14.0 (μA L $mmol^{-1}$)	

GC, glassy carbon electrode; CP, carbon paste electrode; SiO_2/C, carbon–ceramic matrix.

investigated, such as dopamine (DA) and uric acid (UA). Fig. 8A and B shows the CVs and DP responses of the mixture solution of H_2AA, DA and UA in the absence and presence of 5.0×10^{-5} mol L^{-1} ascorbic acid, 1.11×10^{-4} mol L^{-1} dopamine and 5.0×10^{-5} mol L^{-1} uric acid. Fig. 8A, curve (2), shows three broad anodic peaks at 36, 160 and 243 mV obtained by cyclic voltammetry, indicating that H2AA, DA and UA, respectively, are fairly distinguishable at a CA/TiO_2/Sb_2O_5/BQ modified electrode. However, in Fig. 8B, curve (2), as can be observed, there are three well-defined oxidation anodic peaks at −9.3, 120.7 and 199.7 mV. The peak potential separation values of H_2AA and DA, DA and UA, obtained by differential pulse voltammetry, were around 130 mV and 80 mV respectively.

The performance of the CA/TiO_2/Sb_2O_5/BQ modified electrode in comparison with others modified electrodes for the determination for ascorbic acid is shown in Table 1 [65–71]. These results shown that the CA/TiO_2/Sb_2O_5/BQ modified electrode presented good performance with low detection limit and high sensitivity for the differential pulse technique and can be applied to the selective detection of ascorbic acid.

4. Conclusion

The use of supported mixed metal oxides on bio-based materials appears to be an interesting alternative method for the immobilization of electroactive catalysts, since it may combine the advantages of mixed oxides with those of environment- friendly natural biopolymers. The use the proposed modified electrode constructed with particulate mixed oxides such as TiO_2/Sb_2O_5 dispersed inside and outside of the cellulose acetate fiber led to an increase in both sensitivity and selectivity, due to high conductivity combined with ion exchange properties of these metal oxides.

The use of CA/TiO_2/Sb_2O_5/BQ modified electrode for determination of ascorbic acid in pharmaceutical formulations offers some advantages when compared with other methods described in the literature. Moreover, this CA/TiO_2/Sb_2O_5/BQ modified electrode offers many advantages, including simple and rapid preparation, low cost of analysis and high selectivity and sensitivity. These characteristics make this electrode an attractive alternative for application in the analysis of pharmaceutical formulations.

Acknowledgements

The authors are grateful to the Reviewers for the suggestions; to Pró-Reitoria de Pesquisa da Universidade Federal do Rio Grande do Sul (Propesq-UFRGS); to Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS); to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP); to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES); to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq); to Ministério de Ciência e Tecnologia (MCT) for financial support and fellowships. We also thank the CME-UFRGS for the use of the SEM.

References

[1] Y. Gushikem, E.A. Toledo, Preparation of oxide-coated cellulose fiber, in: K. Esumi (Ed.), Polymer Interfaces and Emulsions, Marcel Dekker, New York, 1999, pp. 509–534 (Chapter 13).
[2] Y. Zhang, L. Pan, C. Gao, Y. Wang, Y. Zhao, J. Sol–Gel Sci. Technol. 56 (2010) 27–32.
[3] F. Mizukami, J. Jpn. Petrol. Inst. 51 (2008) 332–347.
[4] A. Walcarius, D. Mandler, J.A. Cox, M. Collinson, O. Lev, J. Mater. Chem. 15 (2005) 3663–3689.
[5] A. Walcarius, Chem. Mater. 13 (2001) 3351–3372.
[6] J. Wang, A. Walcarius, J. Electroanal. Chem. 407 (1996) 183–187.
[7] I. Siro, D. Plackett, Cellulose 17 (2010) 459–494.
[8] S. Richardson, L. Gorton, Anal. Chim. Acta 497 (2003) 27–65.
[9] Z. Yue, I.J. McEwen, J.M.G. Cowie, Solid State Ionics (2003) 155–162.
[10] T. Miyamoto, S. Takahashi, H. Ito, H. Inagaki, Y. Noishiki, J. Biomed. Mater. Res. 23 (1989) 125–133.
[11] N.M. Wara, L.F. Francis, B.V. Velamakanni, J. Membr. Sci. 104 (1995) 43–49.
[12] S. Sourirajan, T. Matsura, Reverse Osmosis and Ultrafiltration, ACS Symposium Series No. 281, American Chemical Society, Washington, DC, 1985.
[13] C.A. Borgo, A.M. Lazarin, Y.V. Kholin, R. Landers, Y. Gushikem, J. Brazil. Chem. Soc. 15 (2004) 47–50.
[14] A.M. Lazarin, C.A. Borgo, Y. Gushikem, Y.V. Kholin, Anal. Chim. Acta 477 (2003) 305–313.
[15] S.A. Nabi, M. Naushad, Colloid Surf. A 316 (2008) 217–225.
[16] G. Splendore, E.V. Benvenutti, Y.V. Kholin, J. Brazil. Chem. Soc. 16 (2005) 147–152.
[17] A.M. Lazarin, R. Landers, Y.V. Kholin, Y. Gushikem, J. Colloid Interface Sci. 254 (2002) 31–38.
[18] A.M. Lazarin, Y. Gushikem, Nitrogen containing organosilicon bonded an Al_2O_3-cellulose acetate hybrid material: preparation, characterization and use for adsorption of Fe(III), Cu(II) and Zn(II) from ethanol solutions, J. Brazil. Chem. Soc. 13 (2002) 88–94.
[19] M. Ali, M. Zafar, T. Jamil, M.T.Z. Butt, Desalination 270 (2011) 98–104.
[20] K. Adachi, T. Mita, S. Tanaka, K. Honda, S. Yamazaki, M. Nakayama, T. Goto, H. Watarai, RSC Adv. 2 (2012) 2128–2136.
[21] E.A. Faria, A.G.S. Prado, React. Funct. Polym. 67 (2007) 655–661.
[22] A.G.S. Prado, E.A. Faria, J.R. Souza De, J.D. Torres, J. Mol. Catal. A-Chem. 237 (2005) 115–119.
[23] S. Chatterjee, S. Sarkar, S.N. Bhattacharyya, Polymer 34 (1993) 1979–1980.
[24] I.W. Shim, W.T. Noh, J. Kwon, J.Y. Cho, K.S. Kim, D.H. Kang, Bull. Korean Chem. Soc. 23 (2002) 563–566.
[25] R. Portela, B. Sánchez, J.M. Coronado, R. Candal, S. Suárez, Catal. Today 129 (2007) 223–230.
[26] R. Liu, H. Ye, X. Xiong, H. Liu, Mater. Chem. Phys. 121 (2010) 432–439.
[27] Y. Ikeda, Y. Kurokawa, K. Nakane, N. Ogata, Cellulose 9 (2002) 369–379.
[28] Y. Ikeda, Y. Kurokawa, J. Biosci. Bioeng. 93 (2002) 98–100.
[29] Y. Ikeda, Y. Kurokawa, J. Sol–Gel Sci. Technol. 21 (2001) 221–226.
[30] Y. Ohmori, Y. Kurokawa, J. Biotechnol. 33 (1994) 205–209.
[31] H. Hatayama, T. Swabe, Y. Kurokawa, J. Sol–Gel Sci. Technol. 7 (1996) 13–17.
[32] S.S. Kelley, J. Filley, A.R. Greenberg, R. Peterson, W.B. Krantz, Int. J. Polym. Anal. Ch. 7 (2002) 162–180.
[33] E.A. Campos, Y. Gushikem, J. Colloid Interface Sci. 193 (1997) 121–126.
[34] G. Arthanareeswaran, P. Thanikaivelan, Sep. Purif. Technol. 74 (2010) 230–235.
[35] G. Arthanareeswaran, T.K.S. Devi, M. Raajenthiren, Sep. Purif. Technol. 64 (2008) 38–47.
[36] G.K. Hyde, S.M. Stewart, G. Scarel, G.N. Parsons, C.-C. Shih, C.-M. Shih, S.-J. Lin, Y.-Y. Su, N.A. Monteiro-Riviere, R.J. Narayan, Biotechnol. J. 6 (2011) 213–223.
[37] N.A. Johari, T.I.T. Kudin, A.M.M. Ali, T. Winie, M.Z.A. Yahya, Mater. Res. Innovations 13 (2009) 232–234.
[38] A.A. Hoffmann, S.L.P. Dias, J.R. Rodrigues, F.A. Pavan, E.V. Benvenutti, E.C. Lima, J. Brazil. Chem. Soc. 19 (2008) 943–949.
[39] A.A. Hoffmann, S.L.P. Dias, E.V. Benvenutti, E.C. Lima, F.A. Pavan, J.R. Rodrigues, R. Scotti, E.S. Ribeiro, Y. Gushikem, J. Brazil. Chem. Soc. 18 (2007) 1462–1472.
[40] A.M. Lazarin, C.A. Borgo, Y. Gushikem, J. Membr. Sci. 221 (2003) 175–184.
[41] C.A. Borgo, A.M. Lazarin, Y. Gushikem, Sens. Actuators B-Chem. 87 (2002) 498–505.
[42] S. Li, W. Yang, M. Chen, J. Gao, J. Kang, Y. Qi, Mater. Chem. Phys. 90 (2005) 262–269.
[43] M.J. Bonne, E.V. Milsom, M. Helton, W. Thielemans, S. Wilkins, F. Marken, Electrochem. Commun. 9 (2007) 1985–1990.
[44] A. Walcarius, Electroanal 13 (2001) 701–718.
[45] M.E. Tess, J.A. Cox, J. Pharmaceut. Biomed. 19 (1999) 55–68.
[46] R. Ojani, J.-B. Raoof, S. Fathi, S. Alami-Valikchali, J. Solid State Electron. 15 (2011) 1935–1941.
[47] A. Walcarius, V. Ganesan, Langmuir 22 (2006) 469–477.
[48] F. Manea, A. Remes, C. Radovan, R. Pode, S. Picken, J. Schoonman, Talanta 83 (2010) 66–71.
[49] A. Walcarius, Electroanal 20 (2008) 711–738.
[50] J. Wang, Anal. Chim. Acta 399 (1999) 21–27.
[51] O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S. Sampath, Chem. Mater. 9 (1997) 2354–2375.
[52] M.I. Vázquez, V. Romero, J. Hierrezuelo, R. Rico, J.M. López-Romero, M.R. López-Ramírez, J. Benavente, J. Membr. Sci. 370 (2011) 70–75.
[53] M.H. Gabr, M.A. Elrahman, K. Okubo, T. Fujii, Compos. Struct. 92 (2010) 1999–2006.
[54] H. Ma, C. Burger, B.S. Hsiao, B. Chu, Biomacromolecules 12 (2011) 970–976.
[55] L.T. Kubota, Y. Gushikem, S. DeCastro, J.C. Moreira, Colloids Surf. 57 (1991) 11–15.
[56] G. Zaitseva, Y. Gushikem, E.S. Ribeiro, S.S. Rosatto, Electrochim. Acta 47 (2002) 1469–1474.
[57] J.E. Gonçalves, Y. Gushikem, S.C. de Castro, J. Non-Cryst. Solids 260 (1999) 125–131.
[58] J.Q. Chambers, Electrochemistry of quinones, in: S. Patai, Z. Rappopor (Eds.), The Chemistry of Quinonoid Compounds, John Wiley & Sons Ltd., New York, 1988, pp. 719–724.
[59] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second ed., Wiley, New York, 2001.
[60] M.A. Kamyabi, Z. Asgari, H.H. Monfared, A. Morsali, J. Electroanal. Chem. 632 (2009) 170–176.

[61] Z. Galus, Fundamentals of Electrochemical Analysis, Ellis Horwood, New York, 1976. pp. 313.
[62] P.R. Lima, P.R.B. Miranda, A.B. Oliveira, M.O.F. Goulart, L.T. Kubota, Electroanal 21 (2009) 2311–2320.
[63] C.R. Silva, J.A. Simoni, C.H. Collins, P.L.O. Volpi, Chem. Educ. 76 (1999) 1421–1422.
[64] E.S. Ribeiro, L.T. Kubota, Microchim. Acta 154 (2006) 303–308.
[65] Y.P. Dong, L. Huang, J. Zhang, X.F. Chu, Q.F. Zhang, Electrochim. Acta 74 (2012) 189–193.
[66] Y. Dai, N. Zhang, D. Wu, J. Yang, J. Zhao, G. Chen, W. Zhao, R. Feng, B. Du, Q. Wei, J. Inorg. Organomet. Polym. 21 (2011) 871–875.
[67] F. Li, J. Li, Y. Feng, L. Yang, Z. Du, Sens. Actuators B-Chem. 157 (2011) 110–114.
[68] T.G.S. Babu, P.V. Suneesh, T. Ramachandran, B. Nair, Anal. Lett. 43 (2010) 2809–2822.
[69] S.A. Kumar, H. Cheng, S. Chen, React. Funct. Polym. 69 (2009) 364–370.
[70] R.F. Castilho, E.B.R. Souza, R.V.S. Alfaya, A.A.S. Alfaya, Electroanal 20 (2008) 157–162.
[71] L.T. Arenas, P.C.M. Villis, J. Arguello, R. Landers, E.V. Benvenutti, Y. Gushikem, Talanta 83 (2010) 241–248.